

# CHAPTER 16 Molecular interactions

## TOPIC 16A Electric properties of molecules

### Discussion questions

**16A.1** Explain how the permanent dipole moment and the polarizability of a molecule arise.

**16A.2** Explain why the polarizability of a molecule decreases at high frequencies.

**16A.3** Describe the experimental procedures available for determining the electric dipole moment of a molecule.

### Exercises

**16A.1(a)** Which of the following molecules may be polar:  $\text{ClF}_3$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ ?

**16A.1(b)** Which of the following molecules may be polar:  $\text{SO}_3$ ,  $\text{XeF}_4$ ,  $\text{SF}_4$ ?

**16A.2(a)** Calculate the resultant of two dipole moments of magnitude 1.5 D and 0.80 D that make an angle of  $109.5^\circ$  to each other.

**16A.2(b)** Calculate the resultant of two dipole moments of magnitude 2.5 D and 0.50 D that make an angle of  $120^\circ$  to each other.

**16A.3(a)** Calculate the magnitude and direction of the dipole moment of the following arrangement of charges in the  $xy$ -plane:  $3e$  at  $(0,0)$ ,  $-e$  at  $(0.32 \text{ nm}, 0)$ , and  $-2e$  at an angle of  $20^\circ$  from the  $x$ -axis and a distance of 0.23 nm from the origin.

**16A.3(b)** Calculate the magnitude and direction of the dipole moment of the following arrangement of charges in the  $xy$ -plane:  $4e$  at  $(0, 0)$ ,  $-2e$  at  $(162 \text{ pm}, 0)$ , and  $-2e$  at an angle of  $30^\circ$  from the  $x$ -axis and a distance of 143 pm from the origin.

**16A.4(a)** The molar polarization of fluorobenzene vapour varies linearly with  $T^{-1}$ , and is  $70.62 \text{ cm}^3 \text{ mol}^{-1}$  at 351.0 K and  $62.47 \text{ cm}^3 \text{ mol}^{-1}$  at 423.2 K. Calculate the polarizability and dipole moment of the molecule.

**16A.4(b)** The molar polarization of the vapour of a compound was found to vary linearly with  $T^{-1}$ , and is  $75.74 \text{ cm}^3 \text{ mol}^{-1}$  at 320.0 K and  $71.43 \text{ cm}^3 \text{ mol}^{-1}$  at 421.7 K. Calculate the polarizability and dipole moment of the molecule.

**16A.5(a)** At  $0^\circ\text{C}$ , the molar polarization of liquid chlorine trifluoride is  $27.18 \text{ cm}^3 \text{ mol}^{-1}$  and its density is  $1.89 \text{ g cm}^{-3}$ . Calculate the relative permittivity of the liquid.

**16A.5(b)** At  $0^\circ\text{C}$ , the molar polarization of a liquid is  $32.16 \text{ cm}^3 \text{ mol}^{-1}$  and its density is  $1.92 \text{ g cm}^{-3}$ . Calculate the relative permittivity of the liquid. Take  $M = 85.0 \text{ g mol}^{-1}$ .

**16A.6(a)** The refractive index of  $\text{CH}_2\text{I}_2$  is 1.732 for 656 nm light. Its density at  $20^\circ\text{C}$  is  $3.32 \text{ g cm}^{-3}$ . Calculate the polarizability of the molecule at this wavelength.

**16A.6(b)** The refractive index of a compound is 1.622 for 643 nm light. Its density at  $20^\circ\text{C}$  is  $2.99 \text{ g cm}^{-3}$ . Calculate the polarizability of the molecule at this wavelength. Take  $M = 65.5 \text{ g mol}^{-1}$ .

**16A.7(a)** The polarizability volume of  $\text{H}_2\text{O}$  at optical frequencies is  $1.5 \times 10^{-24} \text{ cm}^3$ ; estimate the refractive index of water. The experimental value is 1.33; what may be the origin of the discrepancy?

**16A.7(b)** The polarizability volume of a liquid of molar mass  $72.3 \text{ g mol}^{-1}$  and density  $865 \text{ kg m}^{-3}$  at optical frequencies is  $2.2 \times 10^{-30} \text{ m}^3$ ; estimate the refractive index of the liquid.

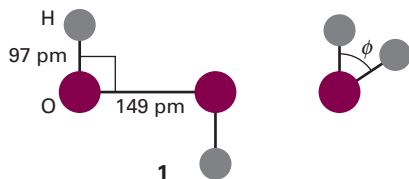
**16A.8(a)** The dipole moment of chlorobenzene is 1.57 D and its polarizability volume is  $1.23 \times 10^{-23} \text{ cm}^3$ . Estimate its relative permittivity at  $25^\circ\text{C}$ , when its density is  $1.173 \text{ g cm}^{-3}$ .

**16A.8(b)** The dipole moment of bromobenzene is  $5.17 \times 10^{-30} \text{ C m}$  and its polarizability volume is approximately  $1.5 \times 10^{-19} \text{ m}^3$ . Estimate its relative permittivity at  $25^\circ\text{C}$ , when its density is  $1491 \text{ kg m}^{-3}$ .

### Problems

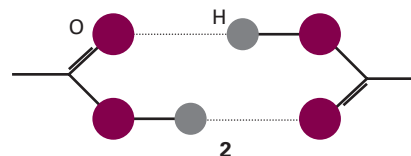
**16A.1** The electric dipole moment of toluene (methylbenzene) is 0.4 D. Estimate the dipole moments of the three xylenes (dimethylbenzene). About which answer can you be sure?

**16A.2** Plot the magnitude of the electric dipole moment of hydrogen peroxide as the  $\text{H}-\text{O}-\text{O}-\text{H}$  (azimuthal) angle  $\phi$  changes from 0 to  $2\pi$ . Use the dimensions shown in 1.



**16A.3** Acetic acid vapour contains a proportion of planar, hydrogen bonded dimers (2). The apparent dipole moment of molecules in pure gaseous acetic

acid has a magnitude that increases with increasing temperature. Suggest an interpretation of this observation.



**16A.4\*** D.D. Nelson et al. (*Science* 238, 1670 (1987)) examined several weakly bound gas-phase complexes of ammonia in search of examples in which the H atoms in  $\text{NH}_3$  formed hydrogen bonds, but found none. For example, they found that the complex of  $\text{NH}_3$  and  $\text{CO}_2$  has the carbon atom nearest the nitrogen (299 pm away): the  $\text{CO}_2$  molecule is at right angles to the C-N 'bond'.

\* These problems were supplied by Charles Trapp and Carmen Giunta

and the H atoms of  $\text{NH}_3$  are pointing away from the  $\text{CO}_2$ . The magnitude of the permanent dipole moment of this complex is reported as 1.77 D. If the N and C atoms are the centres of the negative and positive charge distributions, respectively, what is the magnitude of those partial charges (as multiples of  $e$ )?

**16A.5** The polarizability volume of  $\text{NH}_3$  is  $2.22 \times 10^{-30} \text{ m}^3$ ; calculate the dipole moment of the molecule (in addition to the permanent dipole moment) induced by an applied electric field of strength  $15.0 \text{ kV m}^{-1}$ .

**16A.6** The magnitude of the electric field at a distance  $r$  from a point charge  $Q$  is equal to  $Q/4\pi\epsilon_0 r^2$ . How close to a water molecule (of polarizability volume  $1.48 \times 10^{-30} \text{ m}^3$ ) must a proton approach before the dipole moment it induces has a magnitude equal to that of the permanent dipole moment of the molecule (1.85 D)?

**16A.7** The relative permittivity of chloroform was measured over a range of temperatures with the following results:

$\theta/^\circ\text{C}$	-80	-70	-60	-40	-20	0	20
$\epsilon$	3.1	3.1	7.0	6.5	6.0	5.5	5.0
$\rho/(\text{g cm}^{-3})$	1.65	1.64	1.64	1.61	1.57	1.53	1.50

The freezing point of chloroform is  $-64^\circ\text{C}$ . Account for these results and calculate the dipole moment and polarizability volume of the molecule.

**16A.8** The relative permittivities of methanol (with a melting point of  $-95^\circ\text{C}$ ) corrected for density variation are given below. What molecular information can be deduced from these values? Take  $\rho = 0.791 \text{ g cm}^{-3}$  at  $200^\circ\text{C}$ .

$\theta/^\circ\text{C}$	-185	-170	-150	-140	-110	-80	-50	-20	0	20
$\epsilon_r$	3.2	3.6	4.0	5.1	67	57	49	43	38	34

**16A.9** In his classic book *Polar molecules*, Debye reports some early measurements of the polarizability of ammonia. From the selection below, determine the dipole moment and the polarizability volume of the molecule.

$T/\text{K}$	292.2	309.0	333.0	387.0	413.0	446.0
$P_m/(\text{cm}^3 \text{ mol}^{-1})$	57.57	55.01	51.22	44.99	42.51	39.59

The refractive index of ammonia at 273 K and 100 kPa is 1.000 379 (for yellow sodium light). Calculate the molar polarizability of the gas at this temperature and at 292.2 K. Combine the value calculated with the static molar polarizability at 292.2 K and deduce from this information alone the molecular dipole moment.

**16A.10** Values of the molar polarization of gaseous water at 100 kPa as determined from capacitance measurements are given below as a function of temperature.

$T/\text{K}$	384.3	420.1	444.7	484.1	521.0
$P_m/(\text{cm}^3 \text{ mol}^{-1})$	57.4	53.5	50.1	46.8	43.1

Calculate the dipole moment of  $\text{H}_2\text{O}$  and its polarizability volume.

**16A.11** From data in Table 16A.1 calculate the molar polarization, relative permittivity, and refractive index of methanol at  $20^\circ\text{C}$ . Its density at that temperature is  $0.7914 \text{ g cm}^{-3}$ .

**16A.12** Show that, in a gas (for which the refractive index is close to 1), the refractive index depends on the pressure as  $n_r = 1 + \text{const} \times p$ , and find the constant of proportionality. Go on to show how to deduce the polarizability volume of a molecule from measurements of the refractive index of a gaseous sample.

**16A.13** Acetic acid vapour contains a proportion of planar, hydrogen-bonded dimers. The relative permittivity of pure liquid acetic acid is 7.14 at 290 K and increases with increasing temperature. Suggest an interpretation of the latter observation. What effect should isothermal dilution have on the relative permittivity of solutions of acetic acid in benzene?

## TOPIC 16B Interactions between molecules

### Discussion questions

**16B.1** Identify the terms in and limit the generality of the following expressions: (a)  $V = -Q_2\mu_1/4\pi\epsilon_0 r^2$ , (b)  $V = -Q_2\mu_1 \cos \theta / 4\pi\epsilon_0 r^2$ , and (c)  $V = \mu_2\mu_1(1 - 3 \cos^2 \theta) / 4\pi\epsilon_0 r^3$ .

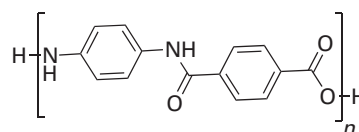
**16B.2** Draw examples of the arrangements of electrical charges that correspond to monopoles, dipoles, quadrupoles, and octupoles. Suggest a reason for the different distance dependencies of their electric fields.

**16B.3** Account for the theoretical conclusion that many attractive interactions between molecules vary with their separation as  $1/r^6$ .

**16B.4** Describe the formation of a hydrogen bond in terms of (a) electrostatic interactions and (b) molecular orbitals. How would you identify the better model?

**16B.5** Account for the hydrophobic interaction and discuss its manifestations.

**16B.6** Some polymers have unusual properties. For example, Kevlar (3) is strong enough to be the material of choice for bulletproof vests and is stable at temperatures up to 600 K. What molecular interactions contribute to the formation and thermal stability of this polymer?



**3** Kevlar

### Exercises

**16B.1(a)** Calculate the molar energy required to reverse the direction of an  $\text{H}_2\text{O}$  molecule located 100 pm from a  $\text{Li}^+$  ion. Take the magnitude of the dipole moment of water as 1.85 D.

**16B.1(b)** Calculate the molar energy required to reverse the direction of an HCl molecule located 300 pm from a  $\text{Mg}^{2+}$  ion. Take the magnitude of the dipole moment of HCl as 1.08 D.

**16B.2(a)** Calculate the potential energy of the interaction between two linear quadrupoles when they are collinear and their centres are separated by a distance  $r$ .

**16B.2(b)** Calculate the potential energy of the interaction between two linear quadrupoles when they are parallel and separated by a distance  $r$ .

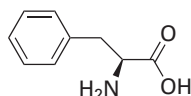
**16B.3(a)** Estimate the energy of the dispersion interaction (use the London formula) for two He atoms separated by 1.0 nm. Relevant data can be found in the *Resource section*.

## Problems

**16B.1** An  $\text{H}_2\text{O}$  molecule is aligned by an external electric field of strength  $1.0 \text{ kV m}^{-1}$  and an Ar atom ( $\alpha' = 1.66 \times 10^{-30} \text{ m}^3$ ) is brought up slowly from one side. At what separation is it energetically favourable for the  $\text{H}_2\text{O}$  molecule to flip over and point towards the approaching Ar atom?

**16B.2** Suppose an  $\text{H}_2\text{O}$  molecule ( $\mu = 1.85 \text{ D}$ ) approaches an anion. What is the favourable orientation of the molecule? Calculate the electric field (in volts per metre) experienced by the anion when the water dipole is (a) 1.0 nm, (b) 0.3 nm, (c) 30 nm from the ion.

**16B.3** Phenylalanine (Phe, 4) is a naturally occurring amino acid. What is the energy of interaction between its phenyl group and the electric dipole moment of a neighbouring peptide group? Take the distance between the groups as 4.0 nm and treat the phenyl group as a benzene molecule. The dipole moment of the peptide group is  $\mu = 2.7 \text{ D}$  and the polarizability volume of benzene is  $\alpha' = 1.04 \times 10^{-29} \text{ m}^3$ .



4 Phenylalanine

**16B.4** Now consider the London interaction between the phenyl groups of two Phe residues (see Problem 16B.3). (a) Estimate the potential energy of interaction between two such rings (treated as benzene molecules) separated by 4.0 nm. For the ionization energy, use  $I = 5.0 \text{ eV}$ . (b) Given that force is the negative slope of the potential, calculate the distance-dependence of the force acting between two non-bonded groups of atoms, such as the phenyl groups of Phe, in a polypeptide chain that can have a London dispersion interaction with each other. What is the separation at which the force between the phenyl groups (treated as benzene molecules) of two Phe residues is zero? (*Hint*: Calculate the slope by considering the potential energy at  $r$  and  $r + \delta r$ , with  $\delta r \ll r$ ,

**16B.3(b)** Estimate the energy of the dispersion interaction (use the London formula) for two Ar atoms separated by 1.0 nm. Relevant data can be found in the *Resource section*.

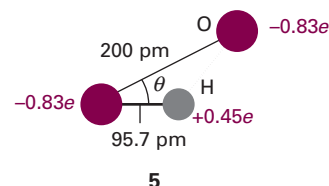
**16B.4(a)** How much energy (in  $\text{kJ mol}^{-1}$ ) is required to break the hydrogen bond in a vacuum ( $\epsilon_r = 1$ )? Use the electrostatic model of the hydrogen bond.

**16B.4(b)** How much energy (in  $\text{kJ mol}^{-1}$ ) is required to break the hydrogen bond in water ( $\epsilon_r \approx 80.0$ )? Use the electrostatic model of the hydrogen bond.

and evaluating  $\{V(r + \delta r) - V(r)\}/\delta r$ . At the end of the calculation, let  $\delta r$  become vanishingly small.)

**16B.5** Given that  $F = -dV/dr$ , calculate the distance dependence of the force acting between two non-bonded groups of atoms in a polymer chain that have a London dispersion interaction with each other.

**16B.6** Consider the arrangement shown in 5 for a system consisting of an O–H group and an O atom, and then use the electrostatic model of the hydrogen bond to calculate the dependence of the molar potential energy of interaction on the angle  $\theta$ .



**16B.7** Suppose you distrusted the Lennard-Jones (12,6) potential for assessing a particular polypeptide conformation, and replaced the repulsive term by an exponential function of the form  $e^{-r/r_0}$ . (a) Sketch the form of the potential energy and locate the distance at which it is a minimum. (b) Identify the distance at which the exponential-6 potential is a minimum.

**16B.8** The *cohesive energy density*,  $\mathcal{U}$ , is defined as  $U/V$ , where  $U$  is the mean potential energy of attraction within the sample and  $V$  its volume. Show that  $\mathcal{U} = \frac{1}{2} \mathcal{N} \int V(R) d\tau$  where  $\mathcal{N}$  is the number density of the molecules and  $V(R)$  is their attractive potential energy and where the integration ranges from  $d$  to infinity and over all angles. Go on to show that the cohesive energy density of a uniform distribution of molecules that interact by a van der Waals attraction of the form  $-C_6/R^6$  is equal to  $(2\pi/3)(N_A^2/d^3 M^2)\rho^2 C_6$ , where  $\rho$  is the mass density of the solid sample and  $M$  is the molar mass of the molecules.

## TOPIC 16C Liquids

### Discussion question

**16C.1** Describe the process of condensation.

### Exercises

**16C.1(a)** Calculate the vapour pressure of a spherical droplet of water of radius 10 nm at  $20^\circ\text{C}$ . The vapour pressure of bulk water at that temperature is  $2.3 \text{ kPa}$  and its density is  $0.9982 \text{ g cm}^{-3}$ .

**16C.1(b)** Calculate the vapour pressure of a spherical droplet of water of radius  $20.0 \text{ nm}$  at  $35.0^\circ\text{C}$ . The vapour pressure of bulk water at that temperature is  $5.623 \text{ kPa}$  and its density is  $994.0 \text{ kg m}^{-3}$ .

**16C.2(a)** The contact angle for water on clean glass is close to zero. Calculate the surface tension of water at  $20^\circ\text{C}$  given that at that temperature water climbs to a height of  $4.96 \text{ cm}$  in a clean glass capillary tube of internal radius  $0.300 \text{ mm}$ . The density of water at  $20^\circ\text{C}$  is  $998.2 \text{ kg m}^{-3}$ .

**16C.2(b)** The contact angle for water on clean glass is close to zero. Calculate the surface tension of water at  $30^\circ\text{C}$  given that at that temperature water

climbs to a height of 9.11 cm in a clean glass capillary tube of internal diameter 0.320 mm. The density of water at 30 °C is 0.9956 g cm<sup>-3</sup>.

**16C.3(a)** Calculate the pressure differential of water across the surface of a spherical droplet of radius 200 nm at 20 °C.

## Problem

**16C.1** The surface tensions of a series of aqueous solutions of a surfactant A were measured at 20 °C, with the following results:

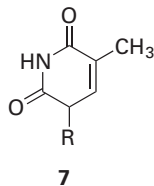
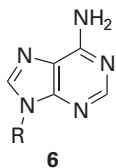
[A]/(mol dm <sup>-3</sup> )	0	0.10	0.20	0.30	0.40	0.50
$\gamma$ /(mN m <sup>-1</sup> )	72.8	70.2	67.7	65.1	62.8	59.8

## Integrated activities

**16.1** Show that the mean interaction energy of  $N$  atoms of diameter  $d$  interacting with a potential energy of the form  $C_6/R^6$  is given by  $U = -2N^2C_6/3Vd^3$ , where  $V$  is the volume in which the molecules are confined and all effects of clustering are ignored. Hence, find a connection between the van der Waals parameter  $a$  and  $C_6$ , from  $n^2a/V^2 = (\partial U/\partial V)_T$ .

**16.2\*** F. Luo et al. (*J. Chem. Phys.* **98**, 3564 (1993)) reported experimental observation of the He<sub>2</sub> complex, a species which had escaped detection for a long time. The fact that the observation required temperatures in the neighbourhood of 1 mK is consistent with computational studies which suggest that  $hc\bar{D}_e$  for He<sub>2</sub> is about  $1.51 \times 10^{-23}$  J,  $hc\bar{D}_0$  about  $2 \times 10^{-26}$  J, and  $R$  about 297 pm. (a) Determine the Lennard-Jones parameters  $r_0$ , and  $a$  and plot the Lennard-Jones potential for He–He interactions. (b) Plot the Morse potential given that  $a = 5.79 \times 10^{10}$  m<sup>-1</sup>.

**16.3** Molecular orbital calculations may be used to predict structures of intermolecular complexes. Hydrogen bonds between purine and pyrimidine bases are responsible for the double helix structure of DNA (see Topic 17A). Consider methyladenine (**6**, with R=CH<sub>3</sub>) and methylthymine (**7**, with R=CH<sub>3</sub>) as models of two bases that can form hydrogen bonds in DNA. (a) Using molecular modelling software and the computational method of your choice, calculate the atomic charges of all atoms in methyladenine and methylthymine. (b) Based on your tabulation of atomic charges, identify the atoms in methyladenine and methylthymine that are likely to participate in hydrogen bonds. (c) Draw all possible adenine–thymine pairs that can be linked by hydrogen bonds, keeping in mind that linear arrangements of the A–H···B fragments are preferred in DNA. For this step, you may want to use your molecular modelling software to align the molecules properly. (d) Consult Topic 17A and determine which of the pairs that you drew in part (c) occur naturally in DNA molecules. (e) Repeat parts (a)–(d) for cytosine and guanine, which also form base pairs in DNA (see Topic 17A for the structures of these bases).

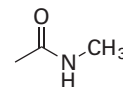


**16.4** Molecular orbital calculations may be used to predict the dipole moments of molecules. (a) Using molecular modelling software and the computational method of your choice, calculate the dipole moment of the peptide link, modelled as a *trans*-*N*-methylacetamide (**8**). Plot the energy of interaction between these dipoles against the angle  $\theta$  for  $r = 3.0$  nm (see eqn 16B.4). (b) Compare the maximum value of the dipole–dipole interaction energy from

**16C.3(b)** Calculate the pressure differential of ethanol across the surface of a spherical droplet of radius 220 nm at 20 °C. The surface tension of ethanol at that temperature is 22.39 mN m<sup>-1</sup>.

Calculate the surface excess concentration.

part (a) to 20 kJ mol<sup>-1</sup>, a typical value for the energy of a hydrogen bonding interaction in biological systems.

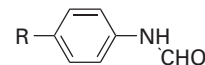


**8** *trans*-*N*-methylacetamide

**16.5** This problem gives a simple example of a quantitative structure–activity relation (QSAR). The binding of nonpolar groups of amino acid to hydrophobic sites in the interior of proteins is governed largely by hydrophobic interactions. (a) Consider a family of hydrocarbons R–H. The hydrophobicity constants,  $\pi$ , for R=CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>, (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, and (CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub> are, respectively, 0.5, 1.0, 1.5, 2.0, and 2.5. Use these data to predict the  $\pi$  value for (CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>. (b) The equilibrium constants  $K_I$  for the dissociation of inhibitors (**9**) from the enzyme chymotrypsin were measured for different substituents R:

R	CH <sub>3</sub> CO	CN	NO <sub>2</sub>	CH <sub>3</sub>	Cl
$\pi$	-0.20	-0.025	0.33	0.5	0.9
log $K_I$	-1.73	-1.90	-2.43	-2.55	-3.40

Plot log  $K_I$  against  $\pi$ . Does the plot suggest a linear relationship? If so, what are the slope and intercept to the log  $K_I$  axis of the line that best fits the data? (c) Predict the value of  $K_I$  for the case R=H.



**9**

**16.6** Derivatives of the compound TIBO (**10**) inhibit the enzyme reverse transcriptase, which catalyses the conversion of retroviral RNA to DNA. A QSAR analysis of the activity  $A$  of a number of TIBO derivatives suggests the following equation:

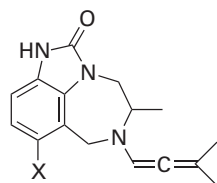
$$\log A = b_0 + b_1S + b_2W$$

where  $S$  is a parameter related to the drug's solubility in water and  $W$  is a parameter related to the width of the first atom in a substituent X shown in **10**. (a) Use the following data to determine the values of  $b_0$ ,  $b_1$ , and  $b_2$ . *Hint:* The QSAR equation relates one dependent variable, log  $A$ , to two independent variables,  $S$  and  $W$ . To fit the data, you must use the mathematical procedure of

multiple regression, which can be performed with mathematical software or an electronic spreadsheet.

X	H	Cl	SCH <sub>3</sub>	OCH <sub>3</sub>	CN	CHO	Br	CH <sub>3</sub>	CCH
log A	7.36	8.37	8.3	7.47	7.25	6.73	8.52	7.87	7.53
S	3.53	4.24	4.09	3.45	2.96	2.89	4.39	4.03	3.80
W	1.00	1.80	1.70	1.35	1.60	1.60	1.95	1.60	1.60

(b) What should be the value of  $W$  for a drug with  $S=4.84$  and  $\log A=7.60$ ?



10